

Chapter 20

Synthesis of Perfluorinated Polyimides for Optical Applications

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This study reports the first synthesis of perfluorinated polyimides that have high Tgs over 270 °C and high optical transparency over the entire wavelengths of optical communications. Their high thermal stability and optical transparency are due to the fully aromatic molecular structure and the absence of hydrogen atoms. The use of diamine, which has relatively high reactivity, and the new per-fluorinated dianhydrides, which has a flexible structure, makes it possible to obtain strong, flexible perfluorinated polyimide film. In addition, these polymers have low dielectric constants, low refractive indices, and low birefringence. Perfluorinated polyimides are promising materials for optical communication applications.

Polymers are expected to be used as media for transmitting near-infrared light in optical communication applications such as waveguides in opto-electronic integrated circuits (OEIC) and in multichip interconnections (1, 2). The current manufacturing process for ICs and multichip modules includes soldering at 260 °C and short-term processes at temperature of up to 400 °C. Waveguide polymeric materials should therefore have high thermal stability—that is, a high glass transition temperature (Tg) and a high polymer decomposition temperature—as well as high transparency at the wavelengths of optical communications (WOC), 1.0–1.7 μm .

Conventional waveguide polymeric materials, such as poly(methyl methacrylate) (PMMA), polystyrene (PS), or polycarbonates (PC), do not have such thermal stability. In addition, their optical losses at the WOC are much higher than in the visible region (0.4–0.8 μm), because carbon–hydrogen (C–H) bonds harmonically absorb infrared radiation. Figure 1 shows the visible-near-infrared absorption spectrum of the PMMA dissolved in chloroform with a concentration of 10 wt%. The same amount of chloroform was used as a reference. Two types of C–H bonds—those in methyl and methylene groups—give broad and strong absorption peaks in the infrared region. Although the wavelengths currently used for long distance optical communication, 1.3 and 1.55 μm , are located in

what are called windows, absorption peaks originating from C-H bonds increase the optical losses at these wavelengths.

Polyimides, on the other hand, have been investigated as optical waveguide materials because they have excellent thermal, chemical and mechanical stability (3-5). We have recently reported new fluorinated polyimides using 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB) as a diamine (6-8). These compounds show high transparency in the visible region as well as low dielectric constants, low refractive indices, and low water absorption. It has been reported that optimally cured partially fluorinated polyimides can be used to decrease optical losses below 0.1 dB/cm in the visible region (at 0.63 μm), and that these losses are stable at temperatures up to 200 °C (5). As described below, however, they also have some absorption peaks in the near-infrared region that originate from the C-H bonds in their phenyl groups.

Figure 2 shows a schematic representation of the fundamental stretching bands and their harmonic absorption wavelengths for the carbon-hydrogen (C-H), carbon-deuterium (C-D), and carbon-fluorine (C-F) bonds. The wavelengths were measured for benzene, hexadeuterobenzene, and hexafluorobenzene with a near-infrared spectrophotometer. For simplicity, we have not shown the absorptions that originate from the fourth and fifth harmonics of the stretching vibration, and from the combinations of the harmonics and the deformation vibration. The harmonics of C-D and C-F bonds are displaced to longer wavelengths than the C-H bond because the wavelengths for the fundamental stretching vibrations of C-D and C-F bonds are about 1.4 and 2.8 times longer than that of C-H bond (9, 10). Since the absorption band strength decreases about one order of magnitude with increase in the order of harmonics (i.e., the vibrational quantum number) (11, 12), the losses in the visible and near-infrared region can be appreciably reduced by substituting deuterium or fluorine for hydrogen atoms. Kaino et al. (13, 14), have produced low-loss optical fibers from deuterated PMMAs and fluorodeuterated PSs. Most recently, Ima-mura et al. (15) fabricated low loss waveguides of less than 0.1 dB/cm at 1.3 μm using deuterated and fluorodeuterated PMMAs. Although this substitution effect must be greater in the near-infrared region, perdeuteration would nonetheless seem inadequate for decreasing optical losses over the entire WOC. The strength of absorption due to the harmonics of C-D bonds is smaller than that due to C-H bonds, but the third harmonics of C-D bond stretching appearing at 1.55 μm (8) are not negligible. On the other hand, perfluorinated amorphous polymers, such as Cytop (Asahi Glass Co.), have been reported to have no absorption peaks between 1.0 and 2.5 μm (16). For the reduction of optical losses in the WOC, perfluorination is, in principle, superior to perdeuteration.

The combination of low optical losses over the entire WOC and high thermal, chemical, and mechanical stability must therefore be attained by the perfluorination of polyimides. In addition, perfluorination should decrease the dielectric constant, refractive index, and water absorption. These characteristics are desirable for optical and opto-electronic applications. This study reports the first synthesis and the properties of perfluorinated polyimides.

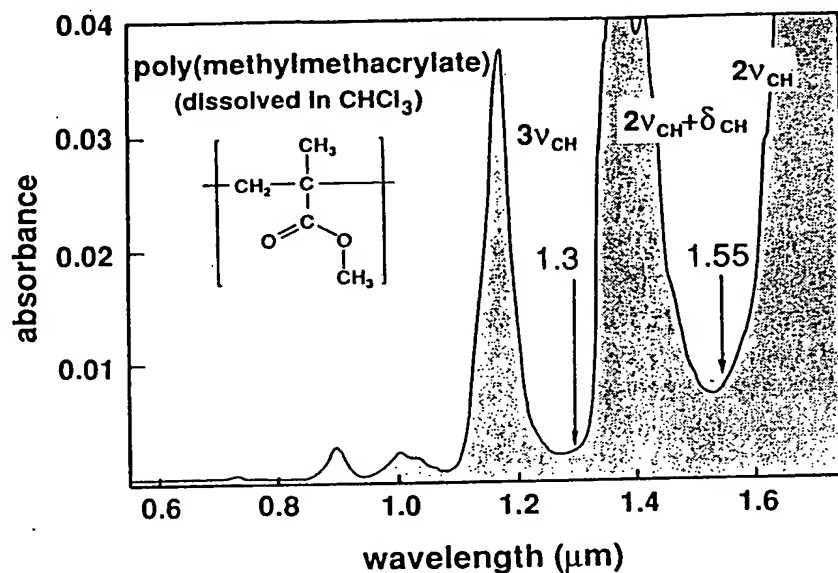


Figure 1. Visible-near-infrared absorption Spectrum of PMMA dissolved in chloroform.

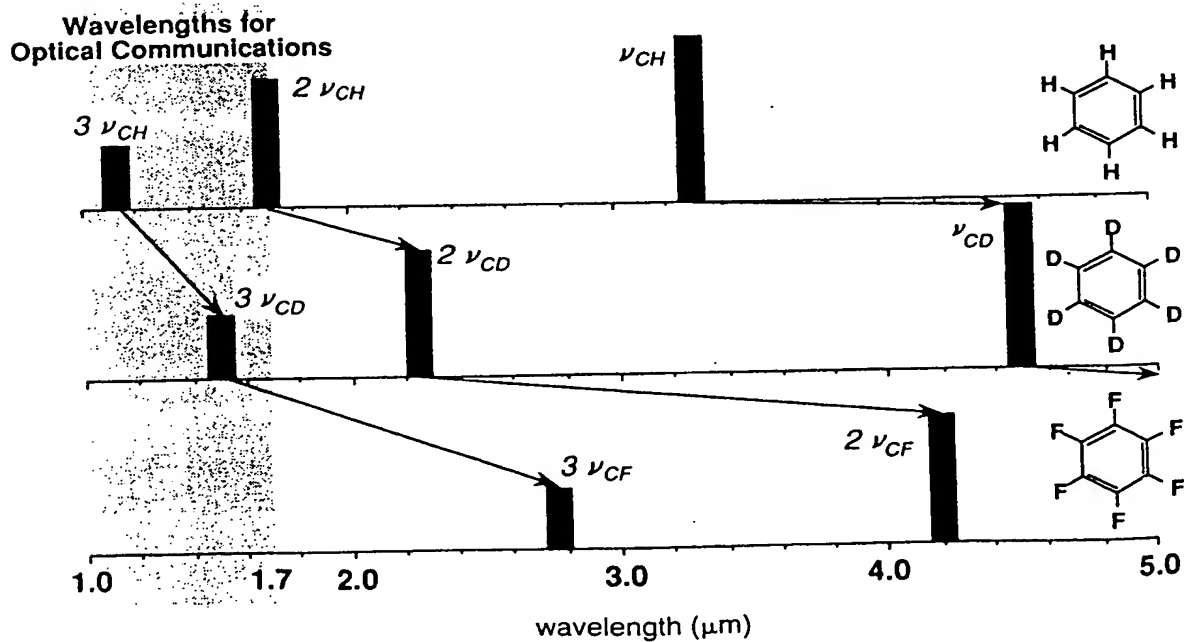


Figure 2. Schematic representation of fundamental stretching bands and their harmonic absorption wavelengths for C-H, C-D, and C-F Bonds.

RESULTS AND DISCUSSION

Figure 3 lists the already known or commercially available perfluorinated dianhydrides and diamines that can be used for synthesizing perfluorinated polyimides. Because of the high electronegativity of fluorine, the substitution of fluorines for hydrogens considerably decreases acylation reactivity of diamine monomers and increases the reactivity of dianhydride monomers. To generate high molecular weight perfluorinated polyimides, it is first necessary to know how fluorine affects the reactivity of the monomers. In particular, the fluorine substituting effect to the diamine reactivity is important because kinetic studies of the acylation of conventional monomers have revealed that acylation rate constants can differ by a factor of 100 between different dianhydrides, and by a factor of 10^5 between different diamines (17).

To estimate the acylation reactivity of perfluorinated diamines, we prepared poly(amic acid)s from the five diamines listed in Figure 3 using 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) as a dianhydride. Table I shows the end-group contents of the poly(amic acid)s determined from ^{19}F NMR. 4FMPD shows the lowest end-group content that means the highest reactivity, and 4FPPD shows the next. However, for all the diamines, the acylations were not complete, and end-group contents were still high even after 6-days reaction. This considerable decrease in reactivity should be induced by the fluorination of diamines. The synthesis of polyimides from perfluorinated diamines and conventional dianhydrides seems fairly difficult even when the most reactive diamine, 4FMPD, is used. When 8FBZ diamine, the least reactive one, was reacted with 6FDA, no NMR signal for the poly(amic acid) could be detected.

In a previous paper (18), we discussed the relationships between the NMR chemical shifts and the rate constants of acylation (k) as well as such electronic-property-related parameters as ionization potential (IP), electronic affinity (EA), and molecular orbital energy for a series of aromatic diamines and aromatic tetracarboxylic dianhydrides. The usefulness of NMR chemical shifts for estimating the reactivity of polyimide monomers was first reported by Okude et al. (19). We have revealed that the ^{15}N chemical shifts of the amino group of diamines (δ_{N}) depend monotonically on the logarithm of k ($\log k$) and on IP.

In this study, we attempted to estimate the reactivity of the five perfluorinated diamines from ^{15}N and ^1H NMR chemical shifts of amino groups (δ_{N} and δ_{H}) and calculated IPs. Figure 4 plots δ_{N} against δ_{H} , where the upfield displacement of chemical shifts (δ_{N} and δ_{H} are decreased) corresponds to the higher reactivity for acylation (18). The IPs calculated using MNDO-PM3 semi-empirical molecular orbital theory (20) are also incorporated in the figure. From the δ_{N} , δ_{H} , and IPs of the diamines, 4FPPD is suggested to have the highest reactivity among the five and 4FMPD is the next. However, this does not coincide with the end-group contents of poly(amic acid)s derived from the experiments described above. As shown in Figure 5, the acylation starts with a nucleophilic substitution in which diamine donates an electron to dianhydride (17). This reaction is called 'first acylation' and it affords a monoacyl derivative (MAD). Poly(amic acid)s are generated by the succeeding 'second acylation', in which MAD reacts with dianhydride, diamine or MAD. Therefore, the reactivity

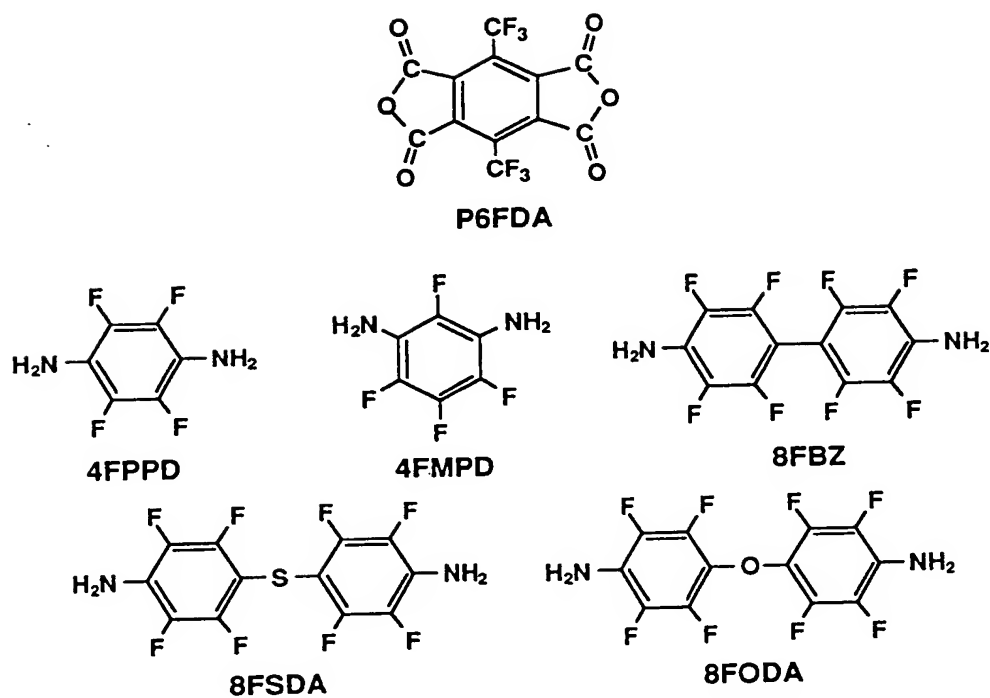


Figure 3. Structures of dianhydride and diamines.

Table I. End-Group Contents of Poly(amic acid)s Synthesized from Perfluorinated Diamines and 6FDA

Diamine	Endgroup Content (%)
4FPPD	42%
4FMPD	15%
8FODA	75%
8FSDA	91%
8FBZ	>99%

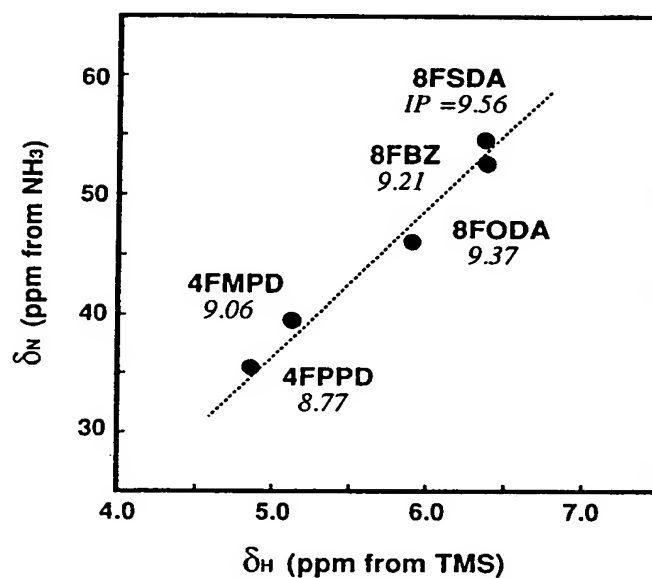
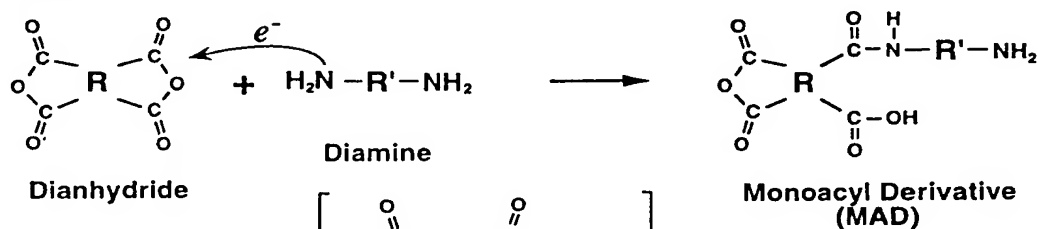


Figure 4. ^{15}N and 1H NMR chemical shifts and calculated ionization potentials (eV) of perfluorinated diamines.

1st. Acylation



2nd. Acylation

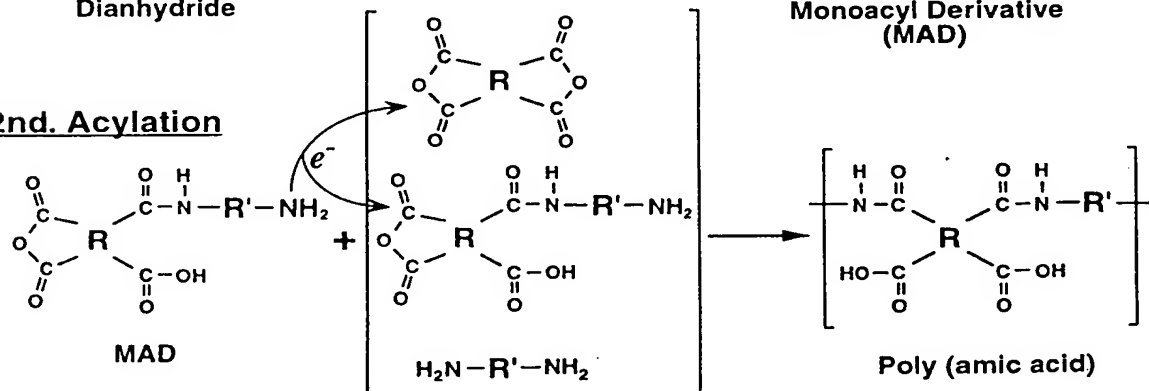


Figure 5. Two-step acylation reactions that generate Poly(amic acid) from diamine and dianhydride.

of MADs rather than that of diamines should be examined for synthesizing high molecular weight poly(amic acid)s.

The five perfluorinated diamines were reacted with equimolar amounts of phthalic anhydride to estimate their MAD reactivity. The molecular structures, δ_N , and δ_H of the diamines and the MADs are shown in Figure 6. The diamine of 8FBZ is not shown because no MAD could be obtained. The δ_N of 4FPPD was displaced downfield by 12.5 ppm in changing to MAD that corresponds to a more than 10^3 decrease of acylation rate constant. On the other hand, the displacements of δ_N and δ_H for the other diamines are much smaller. This means that the reactivity of the residual amino group is little affected by the first acylation, unless two amino groups are located at *para*-position in the same benzene ring. As a result, 4FMPD-MAD shows the highest reactivity that coincides with the result of the end-group content of poly(amic acid)s. Despite the fact that the δ_N and δ_H of 4FPPD-MAD and 8FODA-MAD resonate at near positions, the end group content of the poly(amic acid) derived from 4FPPD and 6FDA was lower than the case of 8FODA and 6FDA (Table I). Some difference may exist in the steric effects during the generation of poly(amic acid)s between one and two benzene ring diamines.

The introduction of fluorine or fluorinated groups into dianhydrides, on the other hand, increases the reactivity. The ^{13}C NMR chemical shift of carbonyl carbons (δ_C) of P6FDA (13), the only existing perfluorinated dianhydride, resonated at about 4 ppm upfield from those of conventional unfluorinated dianhydrides (18). Although δ_C are not as closely correlated with rate constants (18), this upfield shift suggests considerable increase of reactivity. P6FDA is therefore expected to compensate for the low reactivity of perfluorinated diamines.

P6FDA was then used to synthesize perfluorinated polyimides with the five diamines by a conventional method (described in the experimental section). Although P6FDA was suggested to be more reactive than 6FDA, the end-group content of the poly(amic acid) synthesized from 4FMPD and P6FDA was 36% which is higher than that of poly(amic acid) prepared from 4FMPD and 6FDA. The resultant perfluorinated polyimide (P6FDA/4FMPD, Structure 1) was cracked, brittle, and did not form a continuous film. For the other four diamines, the polyimides prepared using P6FDA are coarse powder or films that have many cracks. The primary reason for the non-continuous film is probably that the high reactivity of the perfluorinated dianhydride could not compensate for the very low reactivity of perfluorinated diamines. However, the effect of the rigidity of the polymer chain cannot be neglected for the cases of P6FDA and one-benzene-ring diamines. In this situation, bond rotation is permitted only at the imide linkage (nitrogen-aromatic carbon bonds). However this rotation is restricted by steric hindrance between the fluorine atoms and carbonyl oxygens. The rigidity of the polymer chain has to be improved by introducing flexible linkage groups into the dianhydride component. Accordingly, continuous and flexible films of perfluorinated polyimides are expected to be obtained by combining diamines, which have high reactivities, with dianhydrides, which have flexible molecular structures.

A novel perfluorinated dianhydride, 1,4-bis(3,4-dicarboxytrifluorophenoxy)-tetrafluorobenzene dianhydride (10FEDA), was synthesized according to Scheme

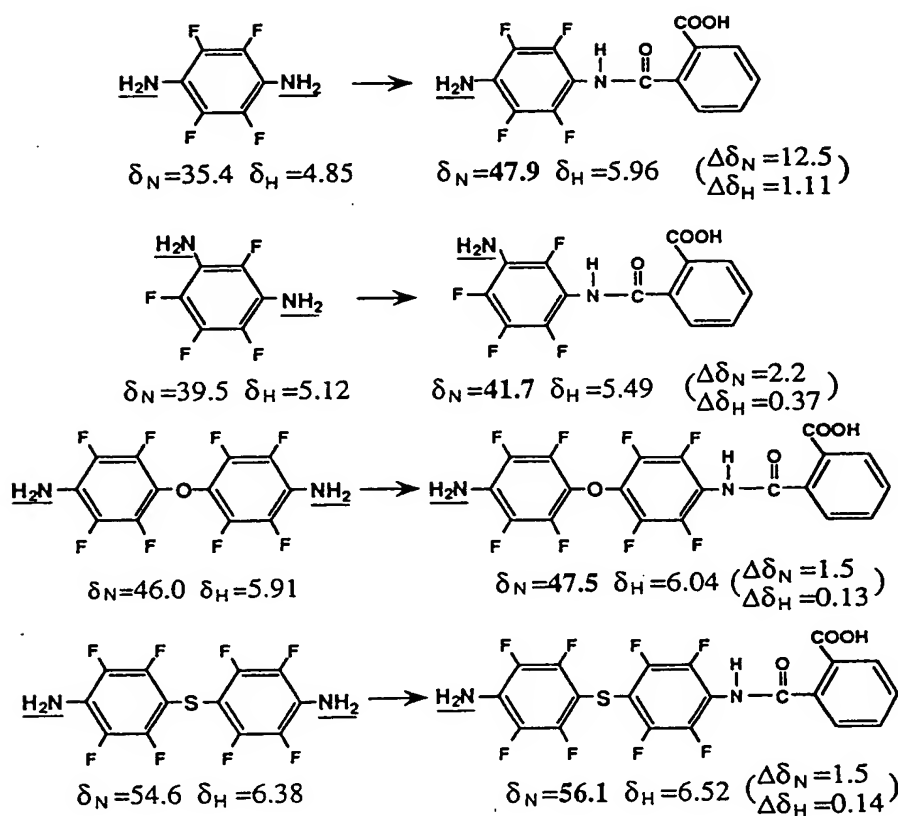
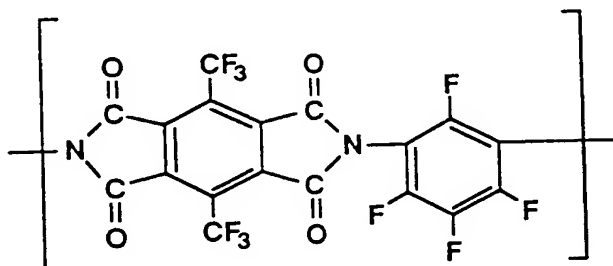
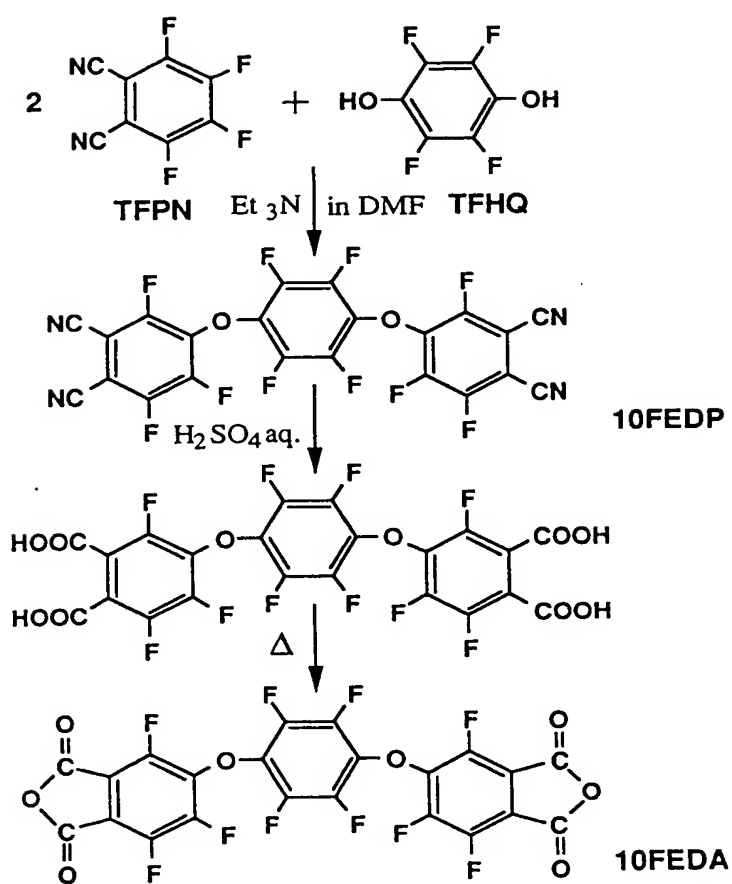


Figure 6. ^{15}N and ^1H chemical shift changes of perfluorinated diamines caused by the first acylation.



Structure 1. P6FDA/4FMPD.

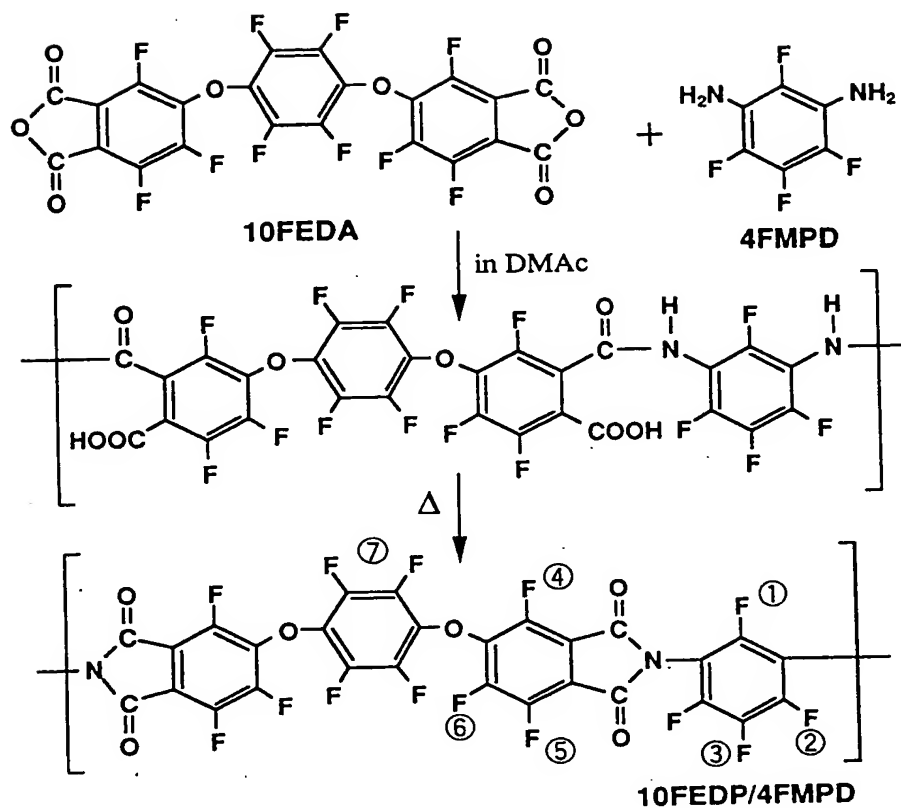


Scheme I.

I. It should be noted that this molecule has two ether-linkages that give flexibility to the molecular structure. In addition, δ_c of 10FEDA (157.5 ppm from TMS) was almost the same as that of P6FDA (157.6 ppm), so this dianhydride should have higher reactivity than unfluorinated and partially fluorinated dianhydrides. The end group content of the poly(amic acid) prepared from 10FEDA and 4FMPD was 6% that is much less than that of poly(amic acid) from P6FDA and 4FMPD (36%). This can be ascribed primarily to the considerable increase of the flexibility of dianhydride structure. The resultant perfluorinated polyimide (10FEDA/4FMPD, Scheme II) was a 9.5- μm thick, strong and flexible film, pale yellow like Dupont's Kapton^R. The film was not soluble in polar organic solvents, such as N-methyl-2-pyrrolidinone (NMP), acetone, N,N'-dimethylformamide (DMF), and N,N'-dimethylacetamide (DMAc). The infrared spectrum of the film (Figure 7) had absorption peaks specific to imide groups (at 1755 cm^{-1} and 1795 cm^{-1}) and no peaks due to C-H bonds (around 3000 cm^{-1}). Thermal mechanical analysis (TMA) showed that the glass transition temperature was 301 °C (Figure 8). This is about 40 degrees higher than the soldering temperature. Thermal gravimetric analysis showed the initial polymer decomposition temperature was 407 °C. At 10 kHz, the dielectric constant of the film was 2.8.

Furthermore, the 10FEDA/4FMPD film cured at 200 °C (stepwise at 70 °C for 2 hours, at 160 °C for 1 hour, and at 200 °C for 2 hours) was soluble in polar organic solvents. The same phenomena have been observed for partially fluorinated polyimides (22). The ^{19}F NMR spectrum of 10FEDA/4FMPD dissolved to a concentration of 5 wt% in acetone- d_6 (Figure 9) also confirmed the completion of imidization at 200 °C. The signals in the spectrum were assigned by using substituent effects determined from model compounds (23). In addition, signals for the end groups of polyimides were under the observation limit. This suggests that polycondensation proceeds during the imidization. The difference in solubility between the polyimides cured at 200 °C and 350 °C may be explained by increased aggregation of the polyimide molecules with curing above T_g , and/or by condensation of unreacted end groups of the polyimide.

The visible-near-infrared absorption spectrum of the 10FEDA/4FMPD, cured at 200 °C and dissolved in acetone- d_6 (10 wt%), is shown in Figure 10. The same amount of acetone- d_6 was used as a reference. The solid line indicates the absorbance of 10FEDA/4FMPD and the dashed line indicates that of partially fluorinated polyimide (6FDA/TFDB (6), Structure 2). Except for a small absorption peak due to moisture (1.4 μm) absorbed in the solvent or adsorbed on the polyimide film, the perfluorinated polyimide has no substantial absorption peak over the entire WOC. Partially fluorinated polyimide, on the other hand, has an absorption peak due to the third harmonic of the stretching vibration of the C-H bond (1.1 μm), a peak due to the combination of the second harmonic of stretching vibration and deformation vibration of the C-H bond (1.4 μm), and a peak due to the second harmonic of the stretching vibration of the C-H bond (1.65 μm). The electronic transition absorption of 10FEDA/4FMPD that appears in the visible region is slightly shifted to longer wavelengths from that of 6FDA/TFDB. This shift causes the yellowish color of 10FEDA/4FMPD but does not affect the transparency in the near infrared region.



Scheme II.

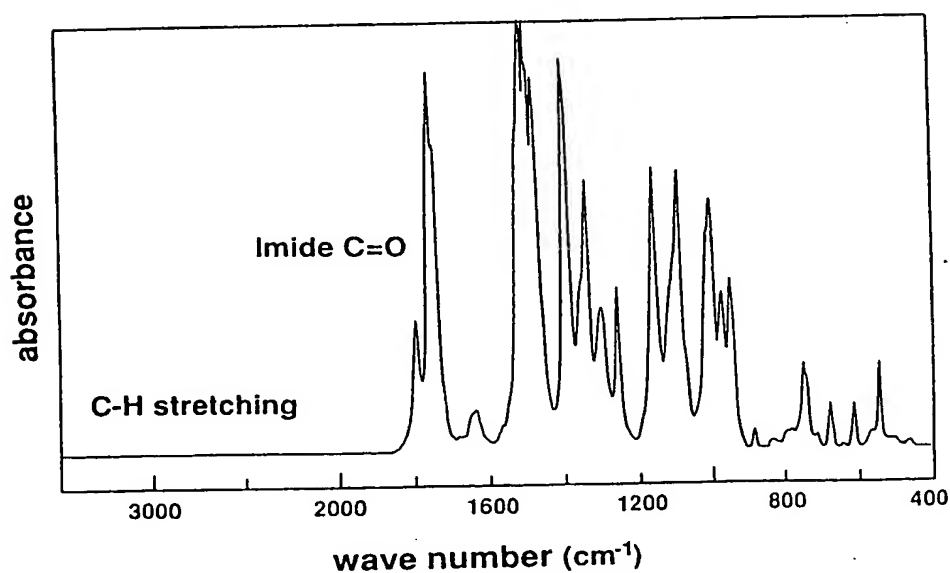


Figure 7. Infrared spectrum of 10FEDA/4FMPD film.

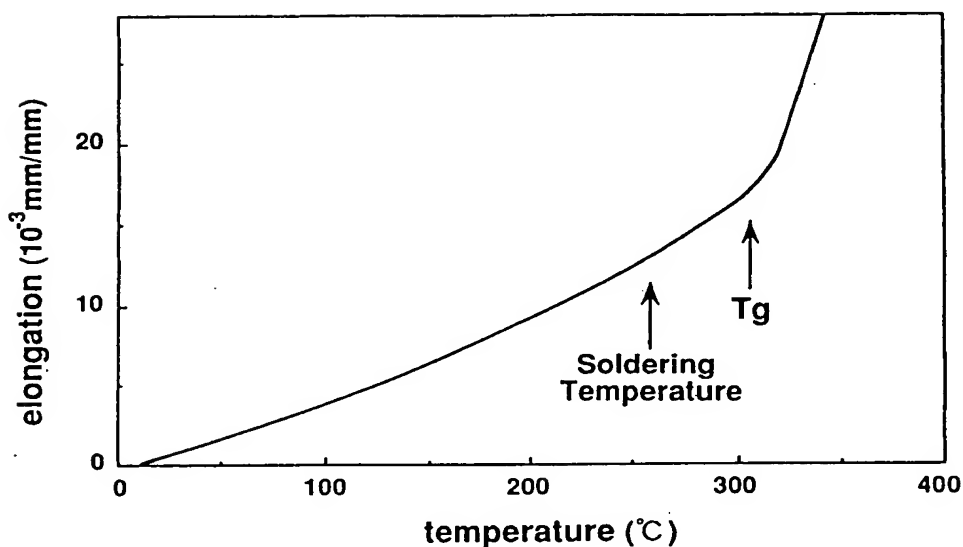
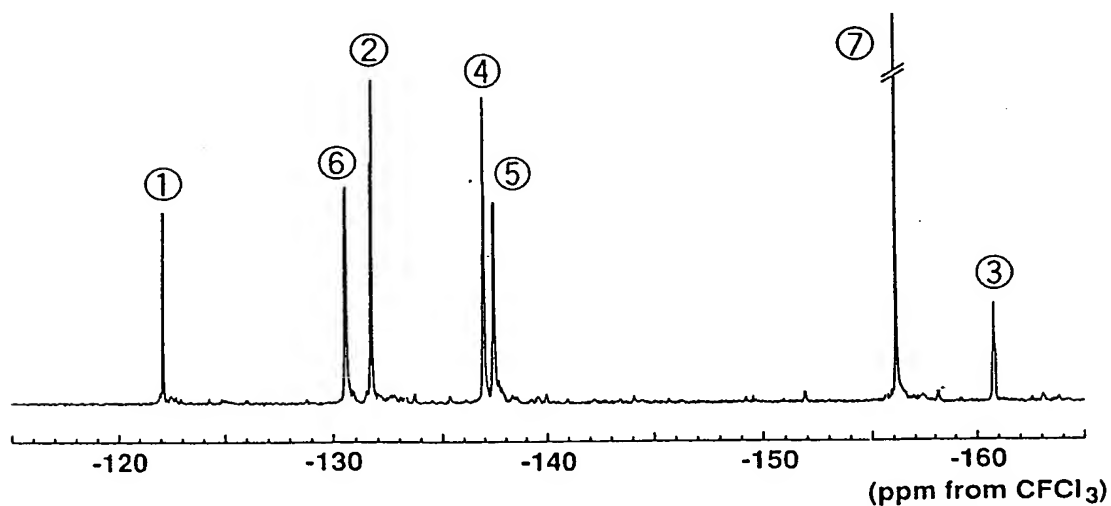


Figure 8. TMA curve of 10FEDA/4FMPD film.

Figure 9. ^{19}F NMR spectrum of 10FEDA/4FMPD dissolved in acetone- d_6 (the numbering of peaks corresponds to the fluorines in Scheme II).

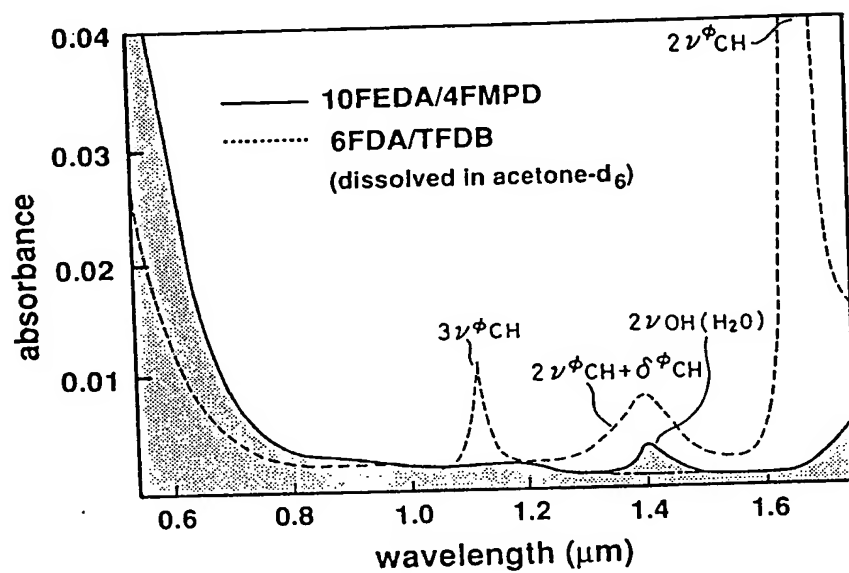
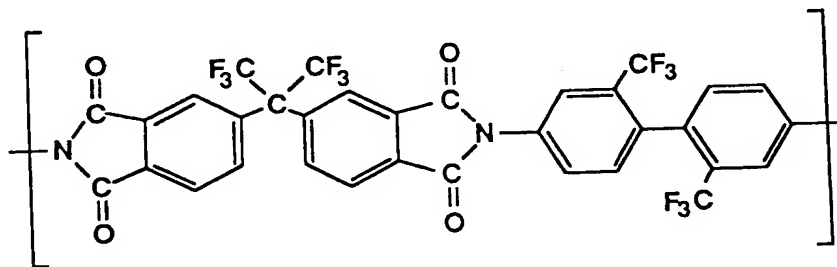


Figure 10. Visible-near-infrared absorption spectrum of 10FEDA/4FMPD and 6FDA/TFDB polyimides dissolved in acetone- d_6 .



Structure 2.

Table II lists the strength and flexibility of perfluorinated polyimide films synthesized from the two dianhydrides and five diamines. Polymerizing 10FEDA with 8FODA or 8FSDA produced continuous and flexible films, but the films were slightly brittle compared with 10FEDA/4FMPD. As described above, P6FDA did not give any continuous films.

Table III lists the properties of perfluorinated polyimides, along with those of partially fluorinated and unfluorinated polyimides. The structure of PMDA/ODA is the same as that of Dupont's Kapton. Because of the direct introduction of fluorines into the aromatic rings and the flexible structure of the 10FEDA component, the polymer decomposition temperatures and Tg's of perfluorinated polyimides are slightly lower than those of conventional polyimides. The thermal stability of these films is nonetheless high enough to withstand the manufacturing process for IC's and multichip modules.

Their dielectric constants (ϵ) at 1kHz and average refractive indices are as low as those of the partially fluorinated polyimides. This is because the fluorine contents of perfluorinated polyimides are comparable to those of partially fluorinated polyimides. It is worth noting that the birefringence of perfluorinated polyimides is lower. This originates from the steric effect between perfluorinated aromatic rings and from a number of bent structures like an ether, a thioether and a *meta*-phenylene linkage. The low birefringence is convenient in designing the waveguide structures in OEICs and in multichip interconnections.

CONCLUSIONS

A novel polymeric material, perfluorinated polyimides, was synthesized. This material is resistant to soldering (260 °C) and highly transparent at the wavelengths of optical communications (1.0-1.7 μm). To generate high molecular weight perfluorinated poly(amic acid)s, the reactivity of five kinds of diamines and their monoacyl derivatives was estimated from the end group content of poly(amic acid), ^{15}N and ^1H NMR chemical shifts, and calculated ionization potential. A new perfluorinated dianhydride, 10FEDA, which has two ether linkages was synthesized in order to provide flexibility to the polymer chain. The perfluorinated polyimides prepared from 10FEDA dianhydride gave flexible films that have Tgs over 270 °C and high optical transparency over the entire optical communication wavelengths. In addition, their dielectric constants and refractive indices are as low as those of conventional fluorinated polyimides, and their birefringence is lower. These characteristics indicate that perfluorinated polyimides are promising materials for optical communication applications.

EXPERIMENTAL SECTION

Materials

We synthesized 1,4-bis(trifluoromethyl)-2,3,5,6-benzenetetracarboxylic dianhydride (P6FDA) (7), and prepared bis(2,3,5,6-tetrafluoro-4-aminophenyl)- ether (8FODA) and bis(2,3,5,6-tetrafluoro-4-aminophenyl)sulfide (8FSDA) according to the schemes reported by Kobrina (24) and Furin (25). Tetrafluoro-*p*-phenyl-

Table II. Strength and Flexibility of Perfluorinated Polyimide Films

<div><div>Dianhydride</div><div>Diamine</div></div>	10FEDA	P6FDA
4FPPD	—	no film
4FMPD	strong and flexible	brittle and cracked
8FODA	flexible	no film
8FSDA	flexible	no film
8FBZ	no film	no film

Table III. Fluorine Contents, Polymer Decomposition Temperatures, Glass Transition Temperatures, Dielectric Constants, Average Refractive Indices, and Birefringences of Perfluorinated, Partially Fluorinated, and Unfluorinated Polyimides

	Fluorine content (%)	Decomp. temp. (°C)	T _g (°C)	ε	\bar{n}	$n_{TE} - n_{TM}$
10FEDA/4FMPD	36.6	501	309	2.8	1.562	0.004
10FEDA/8FODA	38.4	485	300	2.6	1.552	0.004
10FEDA/8FSDA	37.7	488	278	2.6	1.560	<0.01
10FEDA/TFDB	35.1	543	312	2.8	1.569	0.009
6FDA/TFDB	31.3	553	327	2.8	1.548	0.006
PMDA/TFDB	22.7	613	>400	3.2	1.608	0.136
PMDA/ODA	0	608	>400	3.5	1.714	0.088

enediamine (4FPPD) and 4,4'-diaminooctafluorobiphenyl (8FBZ) were obtained from Tokyo Kasei Co. Ltd., and tetrafluoro-*m*-phenylenediamine (4FMPD) was obtained from Fuji Chemical Industries Ltd. These materials were purified by sublimation under reduced pressure.

Preparation of Monoacyl Derivatives (MAD)

The five kinds of perfluorinated diamines listed in Figure 3 were added to tetrahydrofuran (THF) with equimolar amounts of phthalic anhydride to a concentration of 10 wt% and stirred at room temperature for 7 days. The monoacyl derivatives were slowly precipitated and washed by *n*-hexane. From the ^{13}C , ^1H , and ^{19}F NMR, the powder samples thus obtained were mixtures of MAD, diamine, phthalic anhydride, and di(amic acid). However, ^{15}N and ^1H NMR signals of amino groups of MADs were easily assigned. For 8FBZ diamine, no signals of MAD and di(amic acid) was observed.

Synthesis of 10FEDA dianhydride

Tetrafluorophthalonitrile (TFPN) and its half-molar amount of tetrafluorohydroquinone (TFHQ) were stirred at room temperature, in the presence of triethylamine, in dimethylformamide (DMF) as a solvent. This reaction mixture was then poured into water, and the oily lower layer was extracted and washed again with water. This substance was recrystallized from methanol to form 1,4-bis(3,4-dicyanotrifluorophenoxy)-tetrafluorobenzene (10FEDP). The 10FEDP was then stirred in 80% sulfuric acid at 200 °C for 2 hours. After cooling the acid to room temperature, the precipitated white solid was filtered and quickly washed with water, and dried. The chemical shifts and signal ratios observed using ^{19}F NMR spectroscopy were consistent with the assigned structure. A dianhydride of 10FEDA thus obtained was purified by sublimation under reduced pressure.

Preparation of Poly(amic acid)s and Polyimides

Equimolar amounts of a dianhydride and a diamine were added to DMAc to a concentration of 15 wt% and stirred at room temperature for 7 days under nitrogen. The solution of poly(amic acid) was spin-coated onto a silicon wafer and heated first at 70 °C for 2 hours, then at 160 °C for 1 hour, at 250 °C for 30 minutes, and finally at 350 °C for 1 hour.

Measurements

High resolution ^{15}N , ^1H , ^{13}C , and ^{19}F NMR spectra were measured at 40.56, 400.13, 100.61, and 376.49 MHz with a Bruker MSL-400 spectrometer at room temperature (22 °C \pm 2 °C). Samples were dissolved to a concentration of about 6 wt% in dimethylsulfoxide- d_6 (DMSO- d_6). The ^1H and ^{13}C chemical shifts and ^{19}F chemical shift were read directly from internal tetramethylsilane (TMS) and tri-chlorofluoromethane (CFCl_3), respectively. The ^{15}N chemical shifts were

calibrated indirectly through the nitromethane signal (380.4 ppm from NH_3) (26).

The infrared (IR) spectra were measured with a Hitachi 270-30 spectrometer using a silicon wafer as substrate. The visible-near-infrared absorption spectra were measured with a Hitachi U-3400 spectrophotometer using 10 mm quartz cells. The same amount of solvent was used as a reference. The in-plane and out-of-plane refractive indices (n_{TE} and n_{TM}) of the polyimide films were measured with an Atago 4T-Type refractometer at 23 °C. Light from the sodium D-line with a wavelength of 589.3 nm was used, and a polarizer was inserted in the light-path. Average refractive index, \bar{n} , and birefringence were calculated as $(2n_{\text{TE}} + n_{\text{TM}})/3$ and $n_{\text{TE}} - n_{\text{TM}}$, respectively.

The glass transition temperatures (T_g) were measured by thermomechanical analysis (TMA) with a Sinku Riko TMA-7000 analyzer. Specimen dimensions were 5 mm wide, 15 mm long, and 9-15 μm thick. The measurements were carried out during elongation with a heating rate of 5 °C/min under nitrogen at a load of 3 g. The polymer decomposition temperatures were measured by thermogravimetric analysis (TGA) with a Shimadzu TGA-50 analyzer. The measurements were conducted with a heating rate of 10 °C/min under nitrogen.

The dielectric constants were measured with a YHP 4278 capacitance meter at a frequency of 1 kHz and a temperature of 23 °C. Samples were preconditioned at 1 Torr and 120 °C for 2 h to eliminate adsorbed water.

Calculation

Ionization potentials of perfluorinated diamines were calculated as energies of the highest occupied molecular orbitals using the MNDO-PM3 semiempirical molecular orbital approximation (20). Calculations were performed with MOPAC Ver.6 (27) program with a Sony News-830 work station. Bond lengths, bond angles, and dihedral angles were fully optimized within the MNDO-PM3 framework.

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